

Some Thermodynamic and Electrical Properties of Graphite Nitrates

Graphite nitrates of the first, second and third sequences can now be prepared from quite large pieces of near-ideal graphite, by vapor phase nitration. This has permitted some comprehensive studies of various thermal and electrical properties over a wide range of temperatures. Structural studies include measurements of thermal expansion, and of X-ray diffraction. Electrical measurements include resistivity and thermo-electric power (T.E.P.).

Nitration converts graphite to a good metallic conductor with strongly positive T.E.P. This can be interpreted assuming formation of a charge transfer compound with macro-cations formed from the carbon hexagon networks, intercalated by nitrate anions together with nitric acid molecules. An approximate formula for the first sequence compound is $C_{24} + NO_3^-$, $3HNO_3$.

On cooling, crystal compounds of all three sequences show a marked transformation of lambda type at around $-21^\circ C$. X-ray diffraction studies indicate that the intercalated layer passes from liquid-like disorder above the lambda point, to crystal line order below it. This change is progressive over a fairly narrow range of temperatures on either side of the lambda peak. Electrical resistivity measurements show that, as for other good metallic conductors, this property decreases in magnitude as the temperature falls. Around the transition region, marked hysteresis is observed, in a manner characteristic for lambda transformations generally. This can be interpreted in terms of order-disorder influences on the scattering of charge carriers in graphite nitrates. Thermo-electric power of graphite nitrates is even more sensitive to disorder effects than the electrical resistivity. A peak value of T.E.P is observed in the lambda region. Most probably this novel effect arises from scattering of the charge carriers by domains in hybrid crystal structures, such as are likely to be formed in the transition region.